



ORIGINAL ARTICLE

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Fator de enriquecimento  
Lixão do Aurá

## Phytoextraction of heavy metals from a landfill in the metropolitan region of Belém-Pará-Brazil

### *Fitoextração de metais pesados no lixão da região metropolitana de Belém-Pará-Brasil*

**ABSTRACT:** The disposal of municipal waste in open areas constitutes a potential source of environmental risk due to its varied composition, including heavy metals. The endangered areas contain several plant species that may have the potential for use in phytoremediation. The objective of this study was to determine the level of soil contamination by heavy metals and to identify plant species with potential for phytoextraction in the Aurá dump area in the metropolitan region of Belém/PA. The total concentrations of heavy metals in the soil and shoots of five plant species (*Cassia alata*, *Cecropia pachystachya*, *Ipomoea asarifolia*, *Piper hispidinervum* and *Solanum paniculatum*) were determined. The bioconcentration factors of the metals were calculated. The levels of copper (Cu), zinc (Zn), lead (Pb) and cadmium (Cd) were greater than the soil quality reference values for the state of Pará, while the Cd levels were greater than the prevention values established by the National Environmental Council. The concentration of Cd varied among species, from 0.32 mg kg<sup>-1</sup> (*Solanum paniculatum*) to 0.61 mg kg<sup>-1</sup> (*Cassia alata*). *Cassia alata* and *Piper hispidinervum* contained the highest concentrations of Zn, 0.38 and 0.44 mg kg<sup>-1</sup>, respectively. *Cassia alata* exhibited the highest bioconcentration factor for Cd. The disposal of municipal waste in the area contributed to the enrichment of heavy metals in the soil. The predominant plant species in the area were not identified as phytoextractors.

**RESUMO:** A deposição de resíduos urbanos, em áreas a céu aberto, devido a sua composição variada, inclusive de metais pesados, se constitui em fonte potencial de risco ambiental. Nestas áreas ocorrem várias espécies vegetais que podem apresentar potencial para uso na fitorremediação. O objetivo foi determinar o nível de contaminação do solo por metais pesados e identificar espécies vegetais com potencial fitoextrator, na área do lixão do Aurá, região metropolitana de Belém/PA. Foram determinados os teores totais de metais pesados no solo e na parte aérea de cinco espécies vegetais predominantes na área. Foi calculado o fator de bioconcentração de metais. Em média, os teores de cobre (Cu), zinco (Zn), chumbo (Pb) e cádmio (Cd) estão acima dos valores de referência de qualidade dos solos para o estado do Pará, enquanto que os teores de Cd estão acima dos valores de prevenção estabelecido pelo Conselho Nacional de Meio Ambiente. As espécies predominantes foram: *Cassia alata*, *Cecropia pachystachya*, *Ipomoea asarifolia*, *Piper hispidinervum* e a *Solanum paniculatum*. Os valores de bioconcentração de Cd apresentaram maior variação entre as espécies, de 0,32 a 0,61 mg kg<sup>-1</sup>, para *S. paniculatum* e *C. alata*, respectivamente, sendo que as espécies *C. alata* e *P. hispidinervum* apresentaram os maiores valores para Zn, 0,38 e 0,44 mg kg<sup>-1</sup>, respectivamente. A *C. alata* apresentou o maior fator de bioconcentração para o Cd. A deposição do lixo provocou enriquecimento de metais pesados no solo. As espécies predominantes na área não foram identificadas como fitoextratoras.

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## 1 Introduction

Most of the waste produced by mankind continues to be disposed in nature, in landfills or in open dumps. In Brazil, of the 5,564 total municipalities, 60.2% (or 3,352) of municipalities still used improper disposal sites for collected waste in 2012 (ABRELPE, 2012). That level of improper disposal occurred despite the fact that federal law 12.305/2010 remains in force, which specifically addresses the treatment and disposal of municipal solid waste. This law established 2014 as the deadline for the closure of dumps and subsequent recovery of these areas.

The metropolitan region of Belém disposes its solid waste in an area called the Aurá dump. This dump is located within the Aurá River basin, which is the third largest in the metropolitan region and influences the drinking water of the catchment areas (Água Preta and Bolonha water sources) that supply Belém. The disposal of waste in open areas close to water sources can cause significant environmental impacts, such as contamination by organic and inorganic substances. The leachate derived from the disposed waste, which can infiltrate through soil or reach water resources through runoff, is a major concern (Siqueira; Aprile, 2013).

Among environmental pollutants, heavy metals are notable for their high toxicities and long residence times in the environment, posing risks to the biotic components of the surrounding ecosystems even after the closure of dumps (Pastor; Hernández, 2012).

One difficulty associated with determining the contamination level of a dump area is the variability in the heavy metal levels in contaminated soils because waste disposal is irregular in space and time as a result of human action, which can be detected by calculating the metal enrichment factor using the background level for normalization (Becegado et al., 2010).

The term heavy metal generally refers to the various chemical elements with a density greater than  $6 \text{ g cm}^{-3}$ . However, several are metalloids (arsenic) or nonmetals (selenium) that have densities less than  $6 \text{ g cm}^{-3}$  but are included in the heavy metal group because of their toxic effects on the environment (Babula et al., 2008). The term 'heavy metal' was used in this study to represent inorganic substances that can cause environmental contamination. The term "trace element" has also been used in many publications related to this subject.

There are several techniques that have been developed to solve the problem of heavy metal contamination. One of these methods is bioremediation, for which multiple types of organisms are used; when plant species are used, the process is called phytoremediation (Shi et al., 2011). Plants that accumulate heavy metals can be employed in the qualitative and quantitative detection of the stress caused by environmental contamination. However, there is no definite correlation between heavy metal contents in the soil and the contents of these metals in plant tissues (Babula et al., 2008).

One form of phytoremediation is phytoextraction, which uses plant species for the removal of contaminants from the soil because of the ability of a number of plants to absorb metals through their roots and translocate them to their shoots. This is a promising technique to remediate soil contamination and

to prevent contamination of water resources, solving problems caused by waste disposal (Shi et al., 2011). The success of phytoextraction as a potential technology for environmental cleanup depends on several factors. Notably, the form in which a metal is found in the soil and the capacity of a plant to accumulate the heavy metal in its shoots are considered. The plants that have this characteristic are denominated metal accumulators or phytoextractors. However, it is difficult to quantify phytoextraction capacity mainly because *in situ* studies are associated with a range of variables that are difficult to control (Ent et al., 2013).

Alternatively, to identify a plant as a phytoextractor, a bioconcentration factor (BF), which is the ratio of the concentration of a heavy metal in the plant shoot tissue to the concentration of the heavy metal in the soil, is calculated and evaluated. The BF is an important quantitative indicator and has been used to generally estimate the transfer of metals from soils to plants (Chang et al., 2014).

Phytoremediation by itself is already important because it employs plants, which not only decontaminate but also help to restore the degraded area. Using plant species native to the contaminated area is indicated because of their adaptability and because there is evidence of an ecological relationship with the other local organisms (macro and micro).

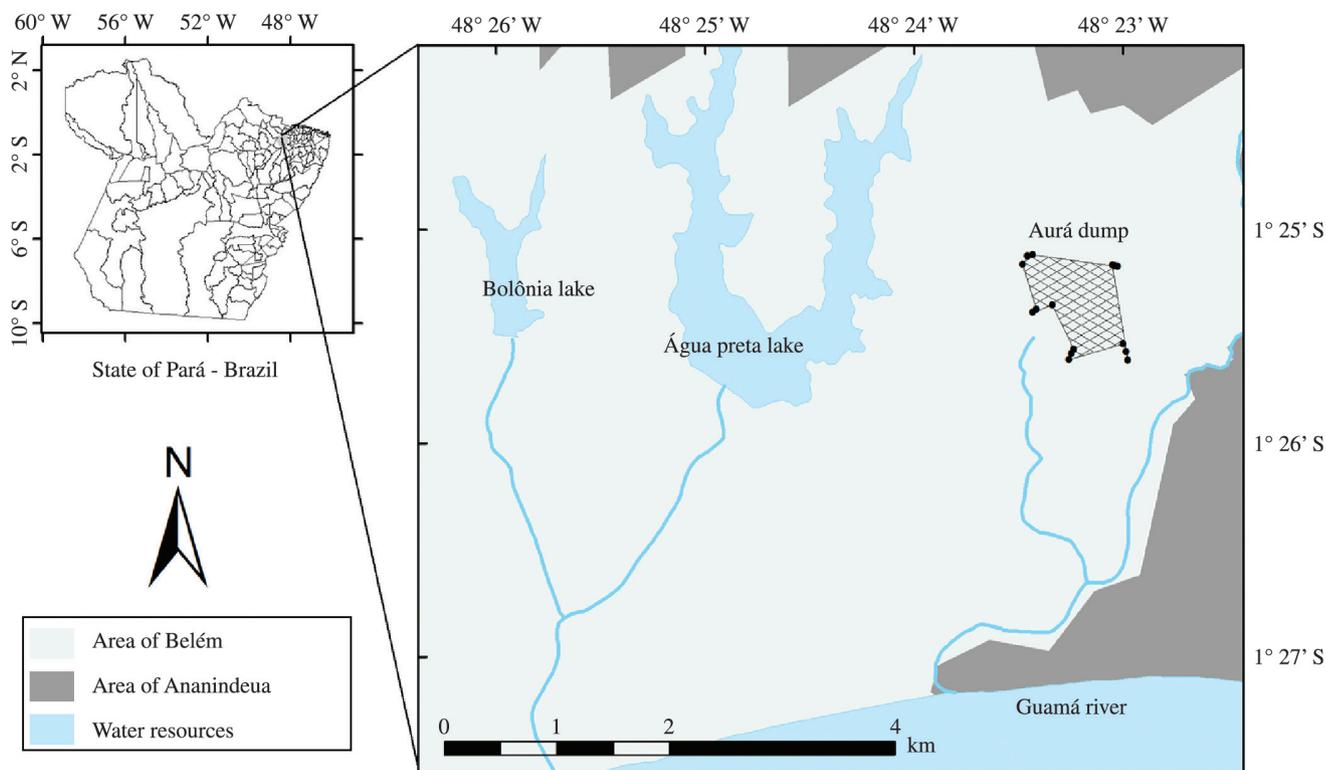
Despite the high biodiversity of the Amazon, there are few studied species, and those with phytoextraction potential are rare. The identification of plants native to the Aurá dump region with phytoextraction capacity will contribute to the understanding of and potential for phytoremediation of the area. Moreover, the characterization of large contaminated areas will enable the government to undertake remedial action to minimize the health risks to the population and the contamination risks to the surrounding ecosystems, including streams that flow into the Guamá River. The objective of this study was to determine the total concentrations of heavy metals and the phytoextraction potentials of plant species found in the area of the Aurá dump.

## 2 Materials and Methods

This study was performed on an area of 100 ha that formed a U shape along the boundary of the Aurá dump, which began operations in 1990. The Aurá dump is located in the Santana de Aurá locality in the Ananindeua municipality ( $1^{\circ} 25' 52''$  S and  $48^{\circ} 23' 16''$  W) of the metropolitan region of Belém, Pará (PA). To the south, lowland areas covered with dense vegetation stretch to the Guamá River; the waste disposal site is located to the north; and the Água Preta lake, which supplies the city of Belém, lies to the west (Figure 1).

The climate of the region is hot and humid, with a high mean annual rainfall (2,800 mm). There are two well-defined rainy periods, one of which is rainier, the other of which is less rainy or dry. The climate is Af according to the Köppen climate classification (Pereira et al., 2002). Oxisols, Plinthosols, Gleysols and Entisols predominate in the study area (Embrapa, 2013). Soil samples were collected in an Oxisol area.

The area was studied by using satellite imagery (LANDSAT TM-5-223\_061) and by visiting the site. Specific sampling sites were determined based on consideration of the size of



**Figure 1.** Location of the study area (Auré dump). Sampling points (•).

**Figura 1.** Localização da área de estudo (Aterro Sanitário de Auré). Pontos de amostragem (•).

the area, vegetation, topography and water resources. Fifteen study sites were established, each with an area of 5 x 25 m, from which samples were collected. Floristic surveys were performed within these sites for the purpose of later choosing the predominant plant species that were studied.

At each sampling point, one composite soil sample was collected, consisting of four single samples collected from a depth of 0-20 cm below the surface. The soil samples were dried in a drying oven at 50 °C for three days. Then, the samples were passed through a 2-mm sieve to remove possible vegetation residues. After homogenization, a sub-sample of the soil was passed through a 0.149-mm sieve (100 mesh).

The EPA 3051 methodology was used for the determination of the concentrations of elemental Fe, Al, Mn, Cu, Cr, Ni, Zn, Cd and Pb in the soil (USEPA, 1994). For this purpose, 0.5 g of oven-dry fine earth (ODFE) were weighed and transferred into high-pressure-modified polyethylene bottles (PTFE); 10 mL of concentrated HNO<sub>3</sub> (65%) was added, and the sample was digested in a microwave (Perkin Elmer, Multiwave 3000). For digestion, 5.5 min of ramping and 4.5 min of a constant temperature of 175 °C with 1400 W of power were used. The obtained extract was transferred to a sterile volumetric flask and the volume was raised to 30 mL with Milli-Q water. The obtained solutions were filtered with quantitative blue-band filter paper (8-mm diameter opening).

Extraction of the available levels of Fe, Al, Mn, Cu, Cr, Ni, Zn, Cd and Pb in the soil was performed with a DTPA solution (pH 7.3). To sterilize the polyethylene volumetric flasks, 10 cm<sup>3</sup> of air-dried fine earth and 20 mL of DTPA

solution were added. The samples were agitated for 2 h in a horizontal agitator at 176 rpm, and the extract was filtered through quantitative blue-band filter paper. The obtained extract was then stored in a new polyethylene volumetric flask (EMBRAPA, 2011). All samples were analyzed in triplicate. The pseudo-total levels and available levels were determined using inductively coupled plasma optical emission spectrometry (ICP – OES) (Perkin Elmer, Optima 3000).

After botanical identification of all species at each sampling point, the five most common native species were selected for further study: two trees, ambay (*Cecropia pachystachya* Trécul) and jurubeba (*Solanum paniculatum* L.); two shrubs, candle bush (*Cassia alata* L.) and long pepper (*Piper hispidinervum* C. DC.); and an herbaceous species, ginger-leaf morning glory (*Ipomoea asarifolia* (Ders.) Roem & Schult). Fully mature leaves from the middle region of the plants were collected. The plant material was packed into plastic bags that had been previously washed with water, and the samples were washed with a nitric acid solution (5%) and ultrapure water. Subsequently, the samples were dried in a forced-air oven at 65 °C for 48 h until they reached a constant weight. The material was ground using a Willey mill (Tecnal) and passed through a 20-mesh sieve.

For the digestion of plant material, 250 mg of each sample was weighed and then placed into a Teflon tube with a screw cap and a pressure-compensating valve. Then, 2 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 30% (v/v) were added. After 2 h, 2 mL of 65% nitric acid (HNO<sub>3</sub>) (MERCK®) were added. The mixture was then subject to cold pre-digestion for 12 h under

a fume hood to decrease the reactivity of the organic matter. After pre-digestion, the sealed tubes containing the samples were placed in a microwave oven (Mars Xpression, CEM Corporation) until total oxidation by heating to 80 °C for 3 min, 150 °C for 5 min and 180 °C for 10 min (Melo et al., 2011). The obtained extracts were filtered and diluted with deionized water in 50 mL plastic flasks to a volume of 30 mL. The Cu, Zn, Cd and Pb concentrations were determined using a flame atomic absorption spectrometer (Varian AA 220, Mulgrave, Victoria, Australia).

From the levels of Al, Fe, Cu, Mn, Zn, Cr, Ni, Cd and Pb measured in the soil, the enrichment factor (EF) was determined for Cu, Mn, Zn, Cr, Ni, Cd and Pb in the analyzed soil using the formula  $EF = (X1/Y1)/(X2/Y2)$ , where X1 is the level of the element in the soil, Y1 is the level of the standard element in the soil, X2 is the natural level (reference value) of the studied element and Y2 is the natural level (reference value) of the standard element (Siqueira; Aprile, 2013). The correlations of Fe and Al with the other metals were evaluated to define the standard element to be used in the normalization of the equation. From the results, Al was chosen.

Considering the variation in heavy metal levels in the soil and that the plants analyzed were not found at all sampling points, the bioconcentration factors (BFs) were evaluated, which relate the heavy metal levels in the plant leaves with the respective levels in the soil at the sampling point where the species was collected. The bioconcentration factor (BF) was determined according to the following formula:

$$BF = MCp/MCs \quad (1)$$

where MCp corresponds to the heavy metal concentration in the plant, and MCs corresponds to the heavy metal concentration in the soil (Chang et al., 2014).

The pH values of the soil were determined in water at a soil:solution ratio of 1:2.5. The organic carbon was determined using the Walkley-Black method (calculation of the organic matter), and the clay content of the soil was determined according to EMBRAPA (2011).

The statistical analysis performed was the Pearson's correlation, using the MINITAB 14 software. For the construction of the bioconcentration factor plots, Microsoft Office Excel 2007 was used. The location map was constructed using ArcGis 9, version 9.3.

### 3 Results and Discussion

The distributions of Al, Fe, Cu, Mn, Zn, Cr, Ni, Cd and Pb across the area of the Aurá dump were quite varied and irregular (Table 1). Ni was not detected at five of the sampling points; the other metals were found at all analyzed sites. Quantitative variations in the heavy metals were observed among the sampling points, and Cr was the element that exhibited the least amount of variation (Table 1). The quantitative and spatial variation among the heavy metals is a result of the disposal of waste at the site.

In a study of the Tarumã-Açu River basin landfill in Manaus (Amazonas), chemical analyses of the water and sediments revealed that the area contains high levels of Zn, Ni, Cr, Fe, Pb and Cu compared to the levels established by Conama and international environmental protection agencies and that there were large variations in concentrations depending on the

**Table 1.** Pseudo-total levels of heavy metals found in the soil at the dump of the Belém, PA metropolitan region.

**Tabela 1.** Pseudototais de metais pesados presentes no solo no aterro da região metropolitana de Belém, PA.

Sampling points	Al			Fe			Cu			Mn			Zn			Cr			Ni			Cd			Pb		
	----- g kg <sup>-1</sup> -----									----- mg kg <sup>-1</sup> -----																	
1	3.2±0.3	11.7±0.9	37.7±3	13.1±0.9	54.9±4.4	23±0.8	0.9±0.1	8.6±0.6	27.8±2.1																		
2	3.1±0.2 <sup>1</sup>	11.6±0.9	35.4±2.8	9.9±0.6	7.2±0.6	23.1±0.9	1±0.1	1.1±0.1	17.6±1.4																		
3	6±0.5	26.6±2.1	28.3±2.3	4.31±0.2	10.6±0.8	23.2±1.6	*	2.1±0.2	10.6±0.7																		
4	4.7±0.4	15.2±1.2	49.9±4	43.5±3.2	145±11.2	23.3±0.8	*	4.7±0.3	60.3±4.8																		
5	10.5±0.8	14.7±1.2	66.8±5.1	76.5±6.1	230±18.4	23.4±1.8	6.7±0.3	3±0.2	44.6±3.6																		
6	18.4±1.6	18.3±1.5	84.2±6.7	115±9.2	173±13.8	23.5±1.9	9.2±0.7	1.3±0.1	95.6±7.4																		
7	4.4±0.3	21.7±1.6	13.6±1.1	45±3.2	34.7±2.8	23.6±0.7	*	2.1±0.1	25.9±2.1																		
8	3.3±0.3	12.1±1	11.6±0.9	19.4±1.6	18.5±1.5	23.7±0.7	*	1.5±0.1	14.2±1.1																		
9	9.4±0.7	10.7±0.8	7.4±0.6	17.9±1.4	18.9±1.6	23.8±0.8	*	1.3±0.1	13.4±1.1																		
10	5.4±0.5	20.8±1.7	41±3.3	98.6±7.2	178±14.1	23.9±1.9	5.2±0.4	2.2±0.2	38±2.8																		
11	5.9±0.4	20.7±1.5	19.6±1.6	8.7±0.7	14.1±1.1	23.1±1.8	1.4±0.1	1.6±0.1	12.8±1																		
12	5.8±0.5	11.4±0.8	1.1±0.1	3.8±0.3	4.8±0.4	23.1±1.8	1.7±0.1	1.1±0.1	9±0.6																		
13	9.3±0.7	18.1±1.4	21.3±1.5	40.8±3.2	48.7±3.9	23.1±0.8	18.1±0.9	1.7±0.1	39.6±3.1																		
14	8.3±0.6	10.9±0.7	10.1±0.7	17.6±1.4	13.1±1	23.1±0.8	2.6±0.2	1.1±0.1	21.7±1.4																		
15	8.4±0.7	13.5±1.1	3.8±0.2	7.5±0.6	15.6±1.2	23.1±1.8	3.2±0.2	1.5±0.1	12.6±0.9																		
RVPará/75 <sup>a</sup>		6.4	0.6	103	7.5	16.4	1.5	0.3	4.5																		
RVPará/90 <sup>b</sup>		7.8	15.7	226	21	35.8	5.2	0.6	6.4																		
Conama <sup>c</sup>			60		300	75	30	1.3	72																		

<sup>1</sup>Values represent the mean±standard deviation (n = 3); <sup>a,b</sup>=Reference values from the state of Pará, 75<sup>th</sup> and 90<sup>th</sup> percentile respectively, determined by the EPA 3051 method (Alleoni et al., 2013); <sup>c</sup> = Prevention values according to Conama 420/2009 (Brasil, 2009). \* not detected.

location of the collection site relative to the landfill (Santana; Barroncas, 2007).

In a deactivated dump in the city of Lages, Santa Catarina, high variability was observed among sampling points and levels of Cd, Cr, Ni, Pb and Hg, although values of Cd were low ( $\leq 0.2 \text{ mg kg}^{-1}$ ) (Becegato et al., 2010). The results attest to the contribution of the dump to environmental contamination, reinforcing the idea that the source of the release of the analyzed heavy metals was likely not of a natural origin.

The level of Mn at point 6 and the levels of the other studied heavy metals at almost all sampling points were above the quality reference values (QRV) established for the state of Pará, considering the 75<sup>th</sup> percentile (Table 1). The levels of Cd at points 4 and 5 were above the prevention value (PV) established by Brazilian legislation, which is  $1.3 \text{ mg kg}^{-1}$ . The concentration at sampling point 1 matched the intervention value (IV) for the residential area, which is  $8 \text{ mg kg}^{-1}$  (Brasil, 2009). This point deserves attention because the IV is the level of the element in the soil above which there are potential direct or indirect risks for human health and is considered to be a concern for general exposure.

The levels of Cu are elevated at point 4 and are worrisome at points 5 and 6, where the concentrations supersede the PV ( $60 \text{ mg kg}^{-1}$ ). At point 6, the Pb concentration is also greater than the PV ( $72 \text{ mg kg}^{-1}$ ) established by Conama. The PV is the concentration limit for a certain substance in the soil above which the soil is unable to sustain its main functions (Brasil, 2009).

At sampling points 4, 5, 6, 7 and 10, the levels of Zn are very elevated, and the levels exceeds the QRV for the state of Pará by ten-fold at point 5, even for the 90<sup>th</sup> percentile, which has a lower rigorous ( $21 \text{ mg kg}^{-1}$ ). The levels of Ni are above the 90<sup>th</sup> percentile reference value for the state of Pará ( $5.2 \text{ mg kg}^{-1}$ ) at points 5, 6, 10 and 13 (Table 1). In general, the levels of the heavy metals analyzed are above the soil quality reference values. This contamination is the result of the frequent disposal of untreated material containing these elements, leading to their accumulation in the soil.

In another study in the Aurá River basin, the mean level of total Cu in the sediments was  $19.57 \pm 4.52 \text{ mg kg}^{-1}$  (Siqueira; Aprile, 2013). This result reinforces the idea that the dump is contributing to the contamination of the site by Cu, most likely because the metal is leaching from the soil to the water source.

Cu is positively correlated with Zn, Cd and Pb, while Zn also exhibited a positive correlation with Pb and Mn. Mn

was positively correlated with Cr, whereas Ni did not exhibit a correlation with any analyzed heavy metal (Table 2). The existence of a positive correlation between two heavy metals indicates that the occurrence of one element at the sampling points analyzed favors the existence, to some extent, of the other element at the same site. In the case of a dump, where material is disposed daily, a positive correlation between two metals can be explained by the sources of contamination, which are most likely the same.

Fe was not correlated with the other heavy metals studied. Therefore, it was not used as a normalization factor in determining the enrichment factor (EF), although many authors choose to use this element because it is considered to be a micronutrient for plants, which can influence the absorption of heavy metals (Christophoridis et al., 2009).

Al was positively correlated ( $p < 0.05$ ) with Mn and Zn ( $p < 0.10$ ) and was utilized as a normalization element for the determinations of EFs. Furthermore, Al is related to the colloidal phase of the soil, its geochemistry resembles the geochemistry of numerous heavy metals and its natural concentration in the environment tends to be uniform (Siqueira; Aprile, 2013). The study area is located in a highly weathered soil; thus, this element plays a major role in influencing the form of binding of heavy metals in the soil. Heavy metal enrichment was found at all of the analyzed sampling points, i.e., EFs  $> 1$  (Table 3). The results indicate an increase in the levels of these elements in the environment caused by the dump, primarily for Cd contamination, which had an extremely high EF (Chen et al., 2007). Moderately severe enrichment was found for Cu at points 1, 2 and 4. At sampling point 4, there was also severe enrichment of Zn, Cd and Pb, while severe EF for Zn was observed at point 10.

There was no Mn enrichment for any of the sampling points, whereas there was weak enrichment for Cr (Chen et al., 2007) at 4 sampling points. The variation in the EFs of Cr is associated with the variation in the Al level because the amount of Cr varied from one point to another. In another study conducted in the Aurá River basin of the metropolitan region of Belém, PA, Siqueira and Aprile (2013) an EF  $> 1$  for Cr observed at various sampling points of water and sediments. The authors attributed the enrichment of metal ions to the leachate derived from the Aurá dump/landfill.

The elevated EFs for the majority of the studied elements demonstrate that the quantities of heavy metals in the soil of the dump in the metropolitan region of Belém are not related to

**Table 2.** Pearson's correlations among the levels of the heavy metals in the dump area in the metropolitan region of Belém, PA.

**Tabela 2.** Correlações de Pearson entre os níveis de metais pesados na área do aterro sanitário da região metropolitana de Belém, PA.

Metals	Fe	Al	Cu	Mn	Zn	Cr	Ni	Cd
<b>Al</b>	0.08							
<b>Cu</b>	0.22	-0.28						
<b>Mn</b>	0.29	0.59**	0.31					
<b>Zn</b>	0.17	0.44*	0.56**	0.88**				
<b>Cr</b>	0.14	0.14	-0.02	0.54**	0.38			
<b>Ni</b>	0.45	0.55	0.01	0.48	0.34	0.22		
<b>Cd</b>	-0.1	-0.31	0.58**	-0.02	0.24	-0.24	-0.19	
<b>Pb</b>	-0.06	-0.02	0.69**	0.33	0.65**	0.04	0.27	0.41

\*Indicates a correlation at the 10% probability level; \*\*indicates a correlation at the 5% probability level.

**Table 3.** Enrichment factors (EFs) of heavy metals in the soil of the dump area in the metropolitan region of Belém, PA and their enrichment status.  
**Tabela 3.** Fatores de enriquecimento (FEs) de metais pesados no solo da área do aterro sanitário da região metropolitana de Belém, PA, e seus níveis de enriquecimento.

Sites	Cu	Mn	Zn	Cr	Ni	Cd	Pb	Enrichment categories*	
1	5.5	0.1	6	1.5	0.4	32.7	9.9		
2	5.3	0.1	0.8	1.5	0.4	4.1	6.5		
3	2.2	0.02	0.6	0.8	-	4.2	2	<b>Value</b>	<b>Status</b>
4	5	0.3	10.9	1.0	-	12.5	14.9	< 1	Not enriched
5	3	0.2	7.7	0.5	0.9	3.5	4.9	1 – 3	Small enrichment
6	2.2	0.2	3.3	0.3	0.7	0.8	6	3 – 5	Moderate enrichment
7	1.4	0.3	2.8	1.1	-	6	6.8	5 – 10	Moderately severe enrichment
8	1.6	0.2	1.9	1.5	-	5.5	4.9	10 – 25	Severe enrichment
9	0.4	0.1	0.7	0.5	-	1.7	1.6	25 – 50	Very severe enrichment
10	3.5	0.6	11.5	0.9	1.4	4.9	8.1	> 50	Extremely severe enrichment
11	1.6	0.05	0.8	0.8	0.3	3.4	2.5		
12	0.1	0.02	0.3	0.8	0.4	2.4	1.8		
13	1.1	0.1	1.8	0.5	2.8	2.3	4.9		
14	0.6	0.1	0.6	0.7	0.4	1.7	3		
15	0.2	0.03	0.7	0.6	0.5	2.2	1.7		

\*Chen et al. (2007).

the rock matrix because in that scenario would suggest EFs < 1 (Chen et al., 2007). Thus, there is evidence that the presence of the dump in the area contributes to soil contamination via the discharge of material containing heavy metals, which corroborates the results obtained by other authors (Siqueira; Aprile, 2013).

In a study designed to compare the EFs for Zn and Cu in Greece between two areas with different contamination levels, Christophoridis et al. (2009) verified that the values determined for the samples from the Bay of Thessaloniki were much greater than the values calculated in samples from the Gulf of Thermaiko. According to the authors, the Gulf of Thermaiko is less polluted, as confirmed by the anthropogenic contribution to the sediment contamination of the bay.

Considering the variation in the levels of heavy metals in the soil and that the plants analyzed were not found at all the sampling points, the bioconcentration factors (BFs) were evaluated, which relate the heavy metal levels in the leaves of the plants to the respective heavy metal levels in the soil at the study site where the species is found.

Cu exhibited the lowest variation in BF values, which ranged from 0.27 to 0.33, whereas Zn and Pb varied from 0.26 to 0.44 and 0.32 to 0.61, respectively. The BF values of Cd varied from 0.26 to 0.43 (Figure 2).

The BF values of Pb were similar to those of Zn for all species. This similarity is related to the positive correlation between these two metals in the soil, which is attributed to the synergism that occurs between these elements, i.e., the presence of one element favors the absorption of the other by the plant (Wu et al., 2010). The species *Cassia alata* and *Piper hispidinervum* exhibited the largest BF values for Pb and Zn.

*Cassia alata* has a greater capacity to transfer soil Cd and to accumulate Cd in its leaves compared to the other species, as demonstrated by its higher BF value. *Solanum paniculatum* exhibited the smallest BF value for Cd (Figure 2).

Studying four plant species and two different sources of heavy metal contamination, Shi et al. (2011) obtained a higher BF for Zn compared to Cu and Pb, regardless of the contamination source and species. Examining the behavior of the heavy metals in six plant species collected in an agricultural area of southern China, the BF of Cd varied from 0.01 to 3.1 and was far greater than the BFs of Cr, Pb, Hg and As (Chang et al., 2014).

In a study to evaluate the BF and plant development of four plant species in contaminated areas, all the plants had BFs < 1, and the species that exhibited the fastest growth was considered to be a good candidate for phytoextraction, establishing that the efficiency of phytoextraction is determined by two main factors: the BF of the heavy metal and the production of biomass (Shi et al., 2011).

The BF of Cd for the species *Solanum paniculatum* was low (Figure 2). The differences in BF among the species indicate that each plant is selective for heavy metals, developing control mechanisms for the absorption of specific heavy metals (Shi et al., 2011).

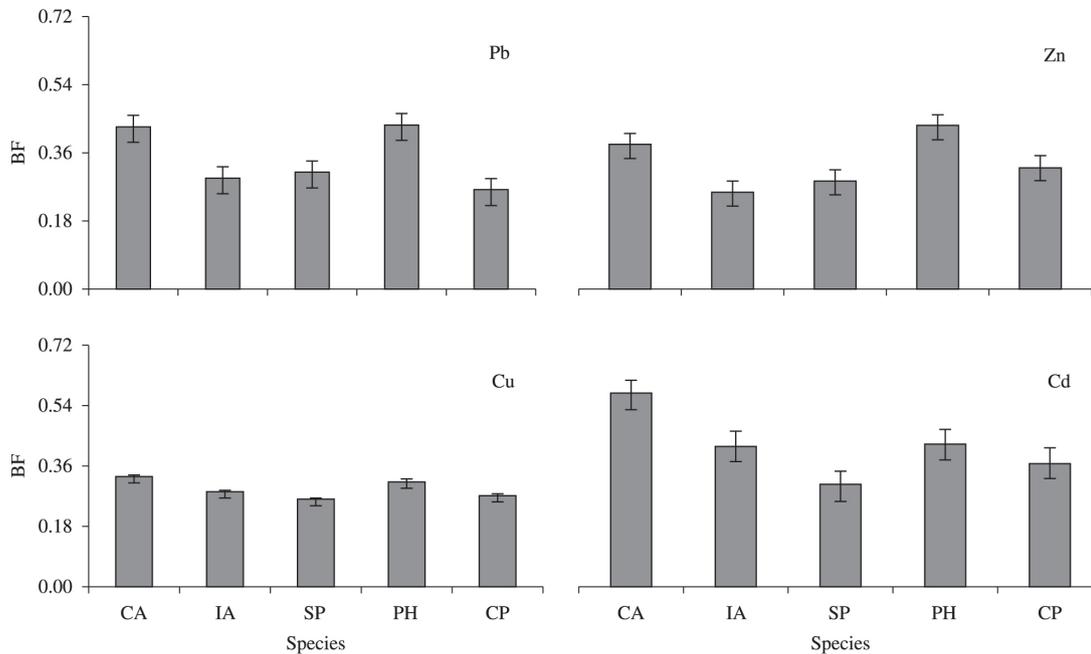
The studied species contained low levels of heavy metals relative to the values of the bioconcentration factors, given that one of the criteria in defining a species as a hyperaccumulator is that the BF be > 1. However, the concentrations of heavy metals present in the tissues of the plants are not the only consideration in the analysis of the potential for a species to be utilized as a phytoextractor. A species must also possess a high growth rate with an elevated biomass production, abundant root system and the ability to absorb/tolerate more than one heavy metal (Ent et al., 2013).

The available Cu levels varied greatly between point 6 (11.8 mg kg<sup>-1</sup>) and point 12 (0.20 mg kg<sup>-1</sup>); there was also high variation for the values of Pb, Zn and Cd (Table 4). This variation may be related to the irregular disposal of solid waste at the study site; however, it is also likely that this variation is

linked to soil factors, such as organic matter and pH, which influence the solubility, mobility and availability of heavy metals to plants (Kabata-Pendias, 2011). The level of organic matter (OM) was relatively low ( $2.6 \text{ dag kg}^{-1}$ ) at point 4 and considerably greater ( $6.4 \text{ dag kg}^{-1}$ ) at point 13; the pH varied

most between points 8 (3.9) and 14 (6.7), while the clay content varied by 6.1% between points 1 and 6 (Table 4).

OM influences the availability of heavy metals because the material synthesized from resistant residues of microbial metabolism or immobilized from live or recently dead cells



**Figure 2.** Bioconcentration factors (BFs) of lead (Pb), zinc (Zn), copper (Cu) and cadmium (Cd) for five plant species: *Cassia alata* (CA), *Ipomoea asarifolia* (IA), *Solanum paniculatum* (SP), *Piper hispidinervum* (PH) and *Cecropia pachystachya* (CP). Mean of three replicates; the bars indicate the standard error of the mean.

**Figura 2.** Fatores de bioconcentração (FBs) de chumbo (Pb), zinco (Zn), cobre (Cu) e cádmio (Cd) para cinco espécies de plantas: *Cassia alata* (CA), *Ipomoea asarifolia* (IA), *Solanum paniculatum* (SP), *Piper hispidinervum* (PH) e *Cecropia pachystachya* (CP). Média de três repetições; as barras indicam o erro padrão da média (EPM).

**Table 4.** Organic matter (OM) and clay contents, pH values, exchangeable levels of Al and available heavy metals in the soil of the dump in the metropolitan region of Belém, PA.

**Tabela 4.** Conteúdos de matéria orgânica (MO) e argila, valores de pH, teores de Al trocável e metais pesados disponíveis no solo do aterro sanitário da região metropolitana de Belém, PA.

Sampling points	pH (H <sub>2</sub> O)	OM		Al	Fe	Cu	Pb	Zn	Cd
		-- dag kg <sup>-1</sup>	-----g kg <sup>-1</sup> ----						
1	6.0±0.4	4.6±0.3	292±20	76.0±5.3	208±14.6	4.2±0.3	3.4±0.2	8.6±0.7	0.7±0.05
2	6.2±0.3*	6.2±0.4	261±18	92.6±6.4	337±23.6	2.3±0.2	3.5±0.2	1.1±0.1	0.1±0.01
3	5.5±0.3	4.1±0.3	272±19	55.1±3.9	255±17.8	3.9±0.3	1.4±0.1	2.6±0.2	0.2±0.01
4	4.9±0.4	2.6±0.2	242±17	19.9±1.4	191±13.6	6.3±0.4	11.7±0.9	17.4±1.3	0.5±0.04
5	5.5±0.4	2.8±0.2	242±17	72.8±5.1	250±17.5	6.4±0.4	4.7±0.3	18.3±1.3	0.2±0.01
6	6.0±0.4	3.0±0.2	232±16	98.5±6.8	248±17.6	11.8±0.8	17.8±1.4	17.6±1.4	0.2±0.01
7	4.2±0.3	3.7±0.3	272±19	16.9±1.4	648±45.4	2.1±0.1	1.8±0.1	6.7±0.5	0.2±0.01
8	3.9±0.3	4.1±0.3	285±21	14.6±1	445±31.2	1.1±0.1	1.5±0.1	1.5±0.1	0.1±0.01
9	5.5±0.2	5.2±0.3	292±20	57.7±4.1	336±23.3	0.4±0.03	0.8±0.1	3.1±0.2	0.1±0.01
10	5.1±0.4	6.2±0.4	242±17	23.0±1.6	121±8.6	5.3±0.4	3.2±0.2	13.4±0.9	0.2±0.02
11	4.0±0.3	5.9±0.4	292±21	45.6±3.2	216±15.1	3.1±0.2	1.5±0.1	2.4±0.2	0.2±0.01
12	5.7±0.4	5.6±0.3	283±18	95.2±6.6	361±25.3	0.2±0.02	1.2±0.1	0.5±0.04	0.2±0.01
13	5.3±0.4	6.4±0.3	258±18	56.4±3.9	123±8.6	4.2±0.3	4.7±0.3	8.1±0.7	0.2±0.01
14	6.7±0.5	6.2±0.4	274±19	79.2±5.5	252±17.7	1.9±0.1	1.4±0.1	1.6±0.1	0.2±0.02
15	5.4±0.3	5.9±0.3	289±22	64.1±4.6	256±17.6	0.5±0.03	0.8±0.1	0.9±0.1	0.1±0.01

\*Values represent the mean±standard deviation (n = 3).

**Table 5.** Pearson's correlation coefficients among pH, and OM and clay contents and the available levels of heavy metals in the soil of the dump in the metropolitan region of Belém, PA.**Tabela 5.** Coeficientes de correlação de Pearson entre os teores de MO e argila, valores de pH e níveis de metais pesados disponíveis no solo do aterro sanitário da região metropolitana de Belém, PA.

	OM	pH	Clay	Al	Fe	Cu	Pb	Zn
pH	0.21							
Clay	0.41	-0.18						
Al	0.19	0.82**	-0.02					
Fe	-0.25	-0.36	0.31	-0.21				
Cu	-0.55*	0.16	-0.81**	0.14	-0.41			
Pb	-0.57*	0.17	-0.75**	0.17	-0.27	0.89**		
Zn	-0.63*	0.03	-0.82**	-0.1	-0.35	0.86**	0.76*	
Cd	-0.3	0.1	0.03	-0.01	-0.29	0.26	0.23	0.37

\*Indicates there was a correlation at the 5% probability level; \*\*indicates a correlation at the 1% probability level.

forms chelates with cations (Prasad, 2003). Moreover, organometallic complexes with polymerized Fe limit the solubilities of heavy metals, and insoluble compounds of high molecular mass can complex heavy metals. OM favors the action of microorganisms, which also act to stabilize heavy metals via processes that include the adsorption of the contaminants to humus by the activities of microbial enzymes (humification) and other mechanisms by which heavy metals are sequestered in the soil (Prasad, 2003).

The soil pH exerts a key role in the availability of heavy metals, favoring adsorption and precipitation when the number of negative charges increases in the soil. The solubility of metallic oxides, mainly the bivalent species, decreases with increasing pH; hence, there are high positive correlations between the coefficients of adsorption of heavy metals (with the exception of Cr and Hg) and the value of soil pH (Souza Braz et al., 2013).

The clay content is negatively correlated ( $p < 0.01$ ) with the levels of Cu, Pb and Zn (Table 5), demonstrating that these metals are adsorbed by inorganic colloids. In weathered soils, such as that considered in this study, with predominantly kaolinitic and oxide mineralogies in the clay fraction, there is an increased affinity of metal cations to the reactive surfaces of these components through physical-chemical reactions (Souza Braz et al., 2013).

The lack of correlation between the available Cd level and the clay content can be explained by the selectivity of the cations to the compounds in the soil; the adsorption selectivity for Cd is always smaller than the selectivity for Cu, Pb and Cr for weathered soils with a predominance of Fe and Al oxides (Souza Braz et al., 2013). This condition can increase the mobility of this element, enabling its movement into water resources. A possible explanation for the differing behavior of Cd relative to Cu and Pb may be associated with the electronic configuration of these metals. The external layers of Cu and Pb possess unpaired electrons, which facilitate the binding and the sharing of electrons, and the empty spaces in the orbitals of these two elements allow the formation of complexes, which is not observed for Cd (Pierangeli et al., 2007).

The OM content is negatively correlated with the available levels of Pb and Zn ( $p < 0.05$ ) (Table 5), demonstrating that these metals can also be bound to the organic fraction of the

soil. The negative correlations of the OM content with Pb and Zn may be related to the formation of organometallic complexes with polymerized Fe or with the insoluble compounds of high molecular mass. Moreover, the positive correlation with available Cu ( $p < 0.05$ ) may be attributed to the formation of chelates from the material synthesized from residues of microbial metabolism or immobilized by material originating from live or recently dead cells (Souza Braz et al., 2013).

The pH was positively correlated ( $p < 0.05$ ) with Al, but there were no significant correlations with any other analyzed metal. pH exerts a key role in the dynamics of the metals, favoring their adsorption, precipitation or availability according to the charge balance of the soil (McBride, 1989). At lower pH values, specific adsorption occurs because the point of zero charge of the Fe and Al oxides is relatively high and positive charges predominate under these conditions, favoring electrostatic adsorption through the formation of outer sphere complexes. With an increase in pH, the Al oxides/hydroxides can become important adsorbers of heavy metals, which precipitate in the structure through the formation of inner sphere complexes. Thus, reactions with high specificity and with the formation of hydrolyzed species occur at higher pH values (McBride, 1989).

Another important aspect is the fact that various plants can exude substances into the rhizosphere, avoiding the absorption and translocation of heavy metals into the shoots through many processes, such as lignification, humification and precipitation, in a process known as phytostabilization (Ali et al., 2013). Therefore, these species can be used for the recovery or revegetation of contaminated areas in programs involving phytostabilization, aiming to minimize the mobilization of the heavy metals in the soil.

## 4 Conclusions

The dump within the metropolitan area of Belém, PA, exhibits soil enrichment with copper, zinc, cadmium and lead as a result of the disposal of waste in the area. The plants studied were not identified as phytoextractors; however, the species *Cassia alata* exhibited the greatest bioconcentration factor for Cd, which suggests some tolerance to the absorption of this element.

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